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Removal of Volatile Aliphatic Hydrocarbons in a Soil Bioreactor

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Soil removal of propane, isobutane and n-butane from a waste air stream was evaluated in the laboratory and in a prototype soil bioreactor. Laboratory investigations indicated first-order kinetics and the potential to degrade light aliphatic hydrocarbons and trichlorethylene, a compound ordinarily resistant to aerobic biological treatment. The predicted behavior of the bioreactor, based on laboratory studies, agreed closely with the actual behavior of the field system. The prototype bioreactor reduced the hydrocarbon concentrations in the air by at least 90 percent with a residence time of 15 minutes and a pressure drop of 85 cm of water. The bioreactor functioned well through a range of temperatures, 12°C to 24°C.

The Clean Air Act, as amended in 1977, mandated the United States Environmental Protection Agency to impose reasonable available control technology (RACT) retroactively upon existing major sources of volatile organic compound (VOC) emissions in areas not meeting the ozone ambient air quality standard.[1] The general goal of most RACT programs is to obtain reductions of VOCs of at least 85 percent. There are explicit methods described in each RACT's Control Techniques Guidelines, but any method which equals or exceeds the required emission reduction is usually acceptable.

A manufacturing facility of S. C. Johnson & Son, Inc. (Johnson Wax) in Racine, Wisconsin, produces a variety of consumer products, some of which are packaged in aerosol cans. During the filling process, some of the aerosol propellant is released. The propellant is a mixture of light hydrocarbons, primarily propane, *n*-butane and isobutane. The filling losses are presently (1986) collected and vented directly to the atmosphere. Although a RACT control has not been developed at the federal level, Johnson Wax anticipates that the state will develop a RACT regulation in the very near future.

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Land treatment is a simple, stable, and cost-effective process for the disposal of a wide variety of industrial waste streams, including vapor-laden air. For example, soil has been used to remove foul-smelling organic compounds from the air of rendering plants.[2] In the presence of adequate oxygen, soils can also oxidize hydrocarbon vapors. Hoeks[3] showed that soils from The Netherlands could degrade as much as 5 milligrams of methane per kilogram of dry soil per hour after a suitable period of acclimation. Ebinger[4] used closed containers of soils to remove added propane at different moistures and temperatures.

Preliminary investigations indicated that biodegradation may be able to satisfy regulatory requirements for the reduction of VOC emissions from aerosol can filling operations. In order to verify the preliminary laboratory VOC destruction efficiencies and determine cold weather effects, Johnson Wax planned construction of a prototype soil bioreactor. After discussion with the Wisconsin Department of Natural Resources, to ensure acceptability of the data obtained from the pilot operation, the bed was constructed. Initial start-up occurred in May of 1984.

At a later date, soil from the prototype bioreactor was provided to the staff of the R. S. Kerr Environmental Research Laboratory (U.S. EPA) for laboratory studies of the kinetics of biodegradation of the individual hydrocarbons in the propellant.

Prototype Soil Bed

The prototype soil bioreactor, Figure 1, was lined with a 0.8-mm reinforced PVC liner to prevent groundwater contamination. (This liner was requested by the Wisconsin Department of Natural Resources to ensure protection of groundwater resources.) The air injection pipes (10-cm Schedule 40 PVC pipe perforated with 3-mm holes) were installed above the liner and buried in Rollin muck soil. This soil contained 6.5 percent organic matter and 45 percent clay and had a pH of 7.4. The surface area of the bed was 190 m^2, and the soil depth was 90 cm. The bottom of the bed was sloped 0.75 percent to carry leachate to a sump. The injected air contained about 2,000 ppm (v/v) total hydrocarbons. The intended flow rate was 3.0 cm^3 air per cm^2 of surface area per min, making the residence time nearly 15 minutes. The pressure drop across the bed was 85 cm of water.

To monitor bed performance, off-gases were collected in a modified fifty-five gallon drum. The drum was open at the bottom, had opposing baffles at the rolling hoops, and had a small vent hole in the top. It was positioned on the soil bed at random, and allowed to come to equilibrium before sampling. Off-gases in the bottom third of the barrel were withdrawn directly into a portable organic vapor analyzer (Foxboro Century OVA model 128 with a flame ionization detector). The influent gas was sampled through a valve on the distribution pipe. The soil temperature was monitored with a thermocouple buried 75 cm in the soil bed.

Laboratory Study

In November, 1985, soil samples from depths of 15, 60, and 90 cm were shipped to the R. S. Kerr Lab for testing. Unused soil from the borrow pile that was used to construct the prototype test bed, was also shipped for use as a control. The soil samples were stored at 12°C and were used within one month of arrival.

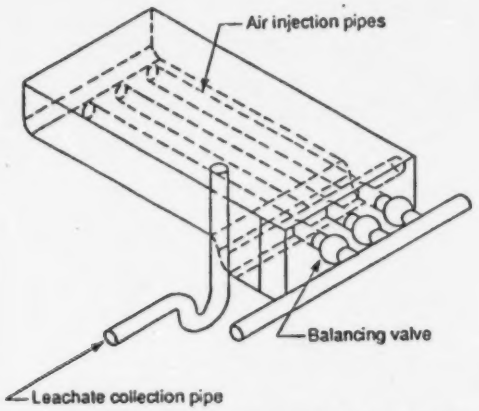

Figure 1. Schematic of the prototype soil bioreactor designed to remove aliphatic hydrocarbon gases from a waste air stream.

Hydrocarbon disappearance was examined in 160-mL glass bottles sealed with Teflon-faced silicone septa and aluminum crimp caps. Each bottle contained 46 g of soil at 30 percent moisture content. The air-filled space in the bottle was about 60 times greater than the air-filled pores of the soil in the prototype bioreactor. The soil was carefully loaded into the bottles to prevent destruction of the water-stable aggregates. Consequently, only the macroporosity was diluted.

The bottles were incubated at room temperature (22–24°). To avoid destroying soil aggregates, the bottles were not shaken or tumbled during experimentation. Propellant gases, supplied by Johnson Wax in an aerosol container, were collected in a gas sampling bulb and injected with a syringe into the bottles through a septum. The propellant mixture was approximately 27 mole percent propane, 29 mole percent isobutane, and 44 mole percent *n*-butane. After appropriate periods of incubation, 100 μL of gas were removed from the bottles with a syringe and analyzed by gas chromatography. The detection limit was 20 and 50 ppm (v/v) for propane and the butanes, respectively.

Laboratory tests were set up in duplicate or triplicate. Calculated rates were obtained by averaging replicates. The rate replicate variation was within ±14 percent, with ±5 percent attributed to GC analysis. The linear regression coefficient (r) for Figure 3 was 0.995, and the precision in determining V_{max} and K_m was near 25 percent.

The soil organisms were exposed to the same hydrocarbon concentrations in both the laboratory and the soil bed. The geometry of the systems necessitated a much larger gas to soil ratio in the laboratory experiments than in the bioreactor. Furthermore, the air flow through the soil in the bioreactor exposed a much larger population of soil organisms to the hydrocarbons. Therefore, biodegradation that required minutes in the prototype bioreactor would be stretched to hours in the laboratory system.

Results and Discussion

Figure 2 shows typical data for the disappearance of propane, *n*-butane and isobutane. Removals were rapid and extensive in the soil from the 60-cm depth in the prototype soil bed, and very slow in the control soil.

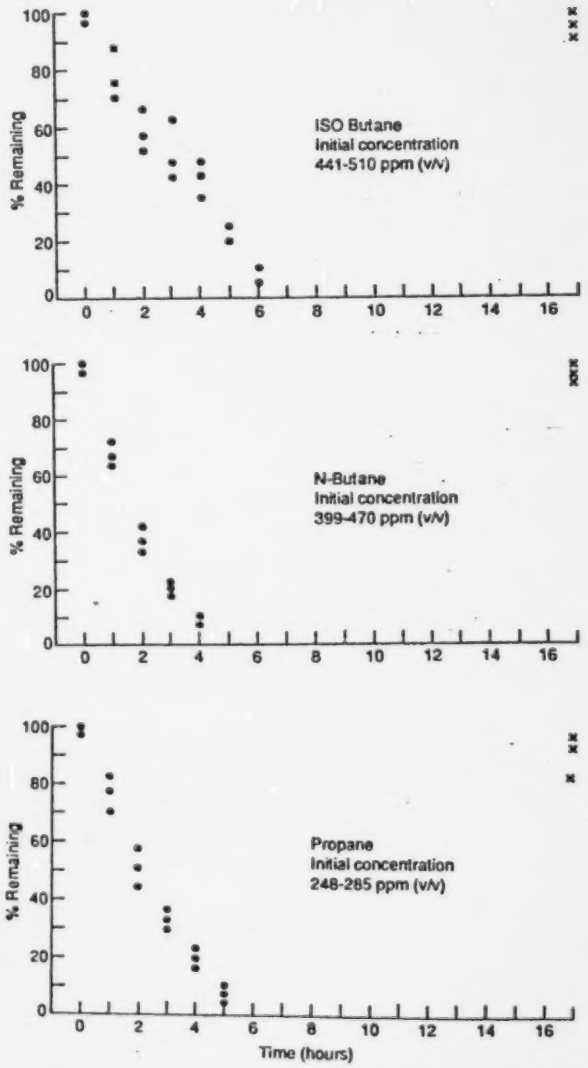

Figure 2. Removal of hydrocarbon vapors by soil: (●) soil from a depth of 60 cm in a prototype bioreactor, (X) control soil not previously exposed to hydrocarbon vapors.

Hydrocarbon disappearance could be due to a variety of mechanisms: sorption to soil components, nonbiological transformations, biodegradation, or leakage from the bottles. We did not attempt to identify the specific removal mechanism in the laboratory control soil tests. However, leakage was not detected from the control bottles.

We expect that previous exposure of the soil to the hydrocarbon vapors should have increased the density of hydrocarbon-degrading bacteria. A comparison of hydrocarbon removal in the control samples to the bioreactor samples strongly supports the conclusion that biodegradation is the primary cause of hydrocarbon disappearance.

The removal rate in replicate bottles was similar. No lag periods or gross changes in this rate were evident. The rate of biodegradation was proportional to the concentration of the organic compound.[5]

At higher concentrations, the biodegradation rate is limited by the microbial capacity to metabolize the organic compound. The rate becomes independent of the organic concentration. This degradation follows a hyperbolic function:

$$1/V = 1/V_{max}\,(1 + K_m/S)$$

where V is the biodegradation rate, V_{max} is the maximum possible biodegradation rate, K_m is an empirical constant representing the concentration where biodegradation shifts from first- to zero-order kinetics (henceforth called the half saturation constant), and S is the concentration of organic compound in air. The removal rate of hydrocarbons was examined at 700, 2000, 6000, and 20000 ppm (v/v) to cover the transition from first- to zero-order kinetics.

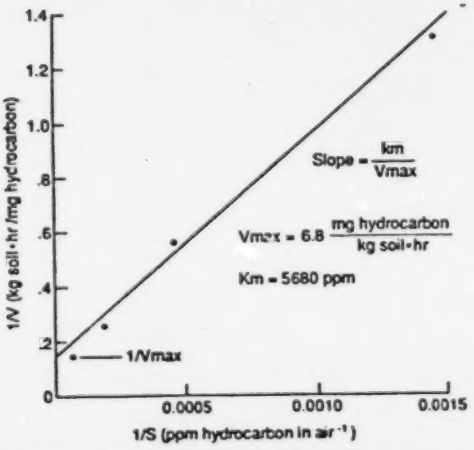

Figure 3. Kinetics of removal of total hydrocarbon vapors by soil from a prototype bioreactor. Lineweaver-Burk plot. Units are expressed in terms of the dry weight of the soil.

The laboratory biodegradation results are presented in a Lineweaver-Burk[6] plot, Figure 3. This is a graphical representation of the kinetics of the bioreactor. Plotted is $1/V$ (1/mg of hydrocarbons per kg of dry soil per hour) versus 1/S (1/ppm). According to this plot, the hydrocarbon degradation follows hyperbolic kinetics. The slope determines the half saturation constant, K_m, which is 5680 ppm. The intercept of the y-axis determines the maximum biodegradation rate for the system, which is 6.8 mg propellant per kg soil per hour. Hydrocarbon removal starting at concentrations roughly an order of magnitude below the half-saturation constant, as in Figure 3, should be described by first-order kinetics.

The soil degradation rates of propane, *n*-butane, and isobutane varied by less than a factor of 3 (Table I). Isobutane disappeared more slowly, as is expected, because branched aliphatic hydrocarbons are usually more difficult to degrade.[7]

The soil biodegradation rate should vary with depth. Soil from a depth of 90 cm in the prototype soil bed experienced the highest concentrations of hydrocarbons and should degrade them fastest. Surprisingly, degradation was much slower in the 90-cm soil. The higher moisture content of this soil may have restricted access of the hydrocarbon propellant to the soil microbes.[6]

The wetness of the soil bioreactor at 90 cm was caused by the liner. If no liner had been used, the soil would have been well-drained at the depth of injection, and the hydrocarbon removal rate would have been similar or superior to that achieved at 60 and 15 cm.

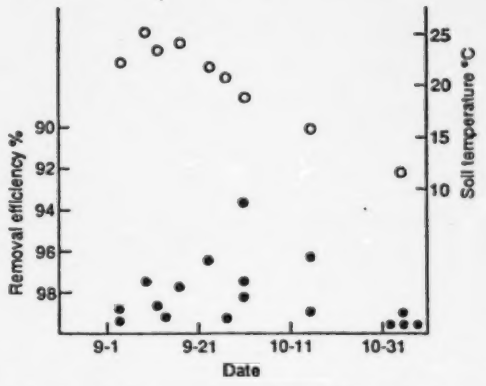

Figure 4. Hydrocarbon removal by a prototype bioreactor: (●) percent of injected concentration biodegraded. (O) soil temperature at the depth of injection.

Wetness also contributed to another operational problem in the soil bioreactor. The flow of gas was restricted. As the pressure gradient increased, the gas flow rate decreased correspondingly. Better drainage of water through the bed, which is dependent upon soil texture, soil composition, leachate collection techniques, and other factors would correct this problem.

The probable intermediates of propane, isobutane and *n*-butane biodegradation are alcohols and ketones. These are produced through hydroxylation of the alkanes by the mono-oxygenase bacterial exzymes which start alkane metabolism.[7] Both alcohols and ketones are readily degradable in oxygenated soil.

Because the oxygen demand of the propellant hydrocarbons is a small fraction of the oxygen in the waste gas injected into the soil, the hydrocarbons degraded completely without any accumulation of the propellant or their transformation products in the leachate collected in the sump. Throughout the two years of operation, the chemical oxygen demand and the concentration of propellant hydrocarbons in the leachate were not significantly higher than the background quality of leachate collected from the soil bioreactor before introduction of any waste gases.

Predicted Behavior of the Soil Bioreactor

The depth-specific degradation rates determined in the laboratory study were used to predict the hydrocarbon concentration at various depths in the bioreactor, as well as the final hydrocarbon concentration released to the atmosphere. The projection of the overall efficiency of the bioreactor was found to be between 95 percent and 99 percent at a soil temperature of 24°C.

Figure 4 shows the hydrocarbon removals by the prototype bioreactor. Laboratory results agreed very well with the bioreactor's results. Field results indicate that the effective-

Table I. Biodegradation of gaseous alkanes in acclimated soil from a bioreactor and in similar soil not previously exposed to alkanes.

Soil	Initial conc. total HC ppm (v/v)	Rate of biodegradation[a] (h^{-1})			
		Propane	Isobutane	*n*-Butane	Total alkanes
Bioreactor 90cm deep	980	0.10	0.039	0.095	0.07
Bioreactor 60cm deep	780	0.45	0.31	0.61	0.39
Bioreactor 15cm deep	1,200	0.39	0.22	0.55	0.35
Control soil	1,400	0.005	0.003	0.003	0.004
Control soil exposed once to hydrocarbons	2,400	0.0041	0.0038	0.0076	0.0054

[a] Rate of biodegradation is the negative of the slope of a linear regression of "the natural logarithm of the fraction of material remaining" on "incubation time." (See Figure 2 for an example.)

ness of the bioreactor was essentially the same at 12°C as at 24°C.

The acclimation time was shown to be slow by laboratory experiment. Several weeks exposure of the control soil to one injection of the propellant hydrocarbons did not increase the degradation rates appreciably, even though the bottles were exposed to relatively large amounts of hydrocarbons.

Hoeks[3] found that soil from the Netherlands required up to 30 days before it degraded natural gas rapidly. Acclimation of the soil in the prototype bioreactor may have been a slow process, resulting in a relatively long start-up time. Johnson's Wax's experience indicates that acclimation requires about 20 days.

Once acclimated, removals of the propellant hydrocarbons were roughly 100 times faster than in soil not exposed to the propellants. See Table I.

Winter Operation of the Bioreactor

One of the goals that led to the construction of the pilot bioreactor was a desire to determine the effects of cold weather on the operation of such a bed. If the bioreactor was to be used as a control method, it would be necessary to obtain substantial reduction of the hydrocarbons throughout the ozone season, if not the entire year.

Temperature concerns were investigated over two Wisconsin winters. As expected, the soil bioreactor ultimately lost most of its ability to degrade VOCs at low temperatures. However, for soil temperatures between 12°C and 24°C, the bioreactor functioned essentially unchanged (Figure 4).

In a discussion of the behavior of soil beds in cold weather, Prokop and Bohn[2] commented on the Johnson Wax prototype soil bed. They reported that the average removal of total volatile organic compounds during the winter of 1984–85 exceeded 90 percent.

The specific temperature where biological activity is diminished has not been determined. However, it appears that biodegradation continues at an acceptable level to meet an 85 percent reduction of incoming hydrocarbons from March to December, even when no effort is made to insulate or heat the bioreactor. If the bed were maintained above a minimum

Table II. Biodegradation of trichloroethylene vapor and gaseous alkanes by soil from a bioreactor acclimated to alkanes.

Soil	Initial conc. ppm (v/v)	Rate of biodegradation[a] h^{-1}
In air		
Trichloroethylene	204	0.37
Propane	830	0.69
Isobutane	550	0.31
n-Butane	610	0.82
In $N_2 + H_2$		
Trichloroethylene	140	0.024

[a] Rate of biodegradation is the negative of the slope of a linear regression of "the natural logarithm of the fraction of material remaining" on "incubation time."

temperature, then satisfactory destruction efficiencies should be maintained all year long, even in severe climates.

Other winter problems were encountered. The two most notable difficulties were obtaining proper temperature measurements in the bed and increased bed pressure resistance due to surface sealing with ice and snow.

Biodegradation of Trichloroethylene

Microorganisms that aerobically metabolize propane can also degrade trichloroethylene.[8] The process is apparently a co-oxidation, since trichloroethylene is not degraded when propane is not available. To determine whether the prototype bioreactor could remove trichloroethylene, a sample of bioreactor soil was loaded into bottles, which were then injected with vapors of propellant hydrocarbons and trichloroethylene.

Trichloroethylene was removed at least as rapidly as the most refractory propellant hydrocarbon (Table II). As a control, the headspace of three bottles was replaced with nitrogen and hydrogen to restrict aerobic metabolism. Removal of trichloroethylene was very slow in the controls. Any removal was probably due to sorption to soil organic matter. Even so, at least 93 percent of the removal in the oxygenated bottles must have been due to aerobic microbial metabolism.

Conclusions

Organic components can be removed from air streams by permeation through soil bioreactors. Soil bioreactors appear to be less expensive than conventional volatile organic compound destruction technologies, such as carbon absorption or incineration.

Further work is needed to identify the most appropriate texture and type of soils for use in bioreactor construction; to determine whether the addition of mineral nutrients will enhance vapor removal; and to find the influence of flow rate, bed depth, organic vapor concentration, and soil moisture content on the rate and extent of organic vapor removal.

This article has not been subjected to U.S. EPA review and does not necessarily reflect the view of the Agency. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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